

Amins war etwas geringer als die des verwendeten HTO, nämlich 14,6 mC/Mol. Aus dem Ausmaß der Verringerung der spez. Akt. läßt sich auf eine Verdünnung der effektiven Tritium-Konzentration in der Schmelze schließen, die wahrscheinlich durch Dissoziation von Wasserstoff aus dem Dimethylaminobenzaldehyd zustande kommt.

H. A. FISCHER, N. SEILER, J. THOBE und G. WERNER

Max-Planck-Institut für Hirnforschung, Arbeitsgr. Neurochemie, Frankfurt/M., BR-Deutschland.

Synthesis and storage of Phenylacetaldehyde (7-¹⁴C)

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Phenylacetaldehyde is an important aroma constituent of roasted peanuts which is most likely generated from Strecker degradation of phenylalanine ⁽¹⁾. Quantitation of this aldehyde in roasted peanut systems via isotope dilution necessitated small amounts of the compound containing a radioactive label. As no evidence was found of phenylacetaldehyde being previously synthesized in this form, we pursued the problem in the following manner: synthesis of the diethylacetal via the Grignard method of Wood and Conley ⁽²⁾, cleavage of the acetal with formic acid ⁽³⁾, and immediate formation of the bisulfite addition product (BAP) for storage. When needed, the aldehyde was regenerated from the BAP with 10 % Na₂CO₃, followed by extraction into carbonyl-free benzene.

1.0 mC Benzyl-7-¹⁴C-chloride (0.1M) was reacted with an equimolar quantity of magnesium turnings under dry ether in the usual manner to form the Grignard reagent. An equimolar quantity of triethylorthoformate was added to the reagent over a period of one hour, followed by five hours of reflux. The ether was removed *in vacuo*. Ice water was added to the system, which was then extracted with ether, adjusted to pH 7.0, and extracted again. The ether was removed from the combined extracts (dried over Na₂SO₄) to yield a crude preparation of ¹⁴C-labeled phenylacetaldehyde diethylacetal (PADEA). Yields of the acetal, obtained by optical quantitation of the 2,4-dinitrophenylhydrazone of phenylacetaldehyde, have fallen most frequently in the range of 13-25 percent.

Vacuum distillation of the crude preparation gave a cut whose properties compared favorably to redistilled commercial phenylacetaldehyde dimethylacetal (PADMA, Eastman). As indicated by Bergman and Pinchas ⁽⁴⁾, acetals

exhibit characteristic infrared absorption bands in the region of 1150-1050 cm^{-1} . PADEA exhibited sharp bands at 1129 and 1065 cm^{-1} ; PADMA showed bands at 1129, 1086, and 1067 cm^{-1} . Both compounds gave strong absorption at 697 cm^{-1} , indicative of a monosubstituted phenyl ring. Gas-liquid chromatograms (cyclohexanedimethanol succinate, Applied Science Labs) of aldehydes regenerated from the bisulfite addition products of acidolyzed PADEA and PADMA (next section) were quite similar in appearance. Reaction of the crude acetal with 2,4-dinitrophenylhydrazine, followed by thin-layer chromatography of the extracted hydrazones, gave indication of phenylacetaldehyde as the only carbonyl present. A contaminant evident on TLC plates was determined as arising from decomposition of the phenylacetaldehyde hydrazone during manipulation.

The acetal was submitted to acidolysis with formic acid according to the procedure of Gorques ⁽⁹⁾. A bath temperature of 90° C with a reaction time of 20-30 minutes appeared appropriate to insure maximum aldehyde recovery. Gorques recommended evaporation of excess formic acid before reaction with bisulfite, but we found direct addition of 50 ml sodium bisulfite reagent (pH 6.8-7.0) to the reaction mixture was most successful. After standing overnight, the precipitate was filtered under vacuum, washed with absolute ethanol, and finally ethyl ether. Following a short period of air-drying, the material was intimately ground and stored in a CaCl_2 -desiccator at room temperature.

Impurities associated with commercially-available sodium bisulfite appeared to catalyze instability in the bisulfite addition product. Thus, the bisulfite reagent was prepared by bubbling SO_2 gas into NaOH solution to the proper pH. Absolute ethanol was added to the cloud point. Following removal of the small quantity of precipitate by filtration, the reagent was ready for use.

Carbonyl analyses ⁽⁵⁾ of the isolated addition product indicated approximately 25 % was pure BAP; therefore, considerable unreacted bisulfite must have precipitated from solution along with the addition product.

The adduct has been stored over several months. There is some fluctuation in specific activity, which is attributed primarily to the fact that the carbonyl analyses of the BAP were made on a microgram basis, while radioactive monitoring was performed on the milligram level. The aldehyde appeared to maintain a high level of activity during storage with a loss of slightly over 10 %.

Phenylacetaldehyde is sensitive to oxidation and polymerization. Attempts to stabilize commercially-available, unlabeled phenylacetaldehyde using such agents as alcohols (isopropyl, benzyl, phenylethyl), esters (diethyl phthalate, benzyl benzoate), and tartaric acid ⁽⁶⁻⁸⁾ have proven less than successful. We have found our procedure for storage of small quantities of the labeled aldehyde with high specific activity to be quite satisfactory.

W. Y. COBB

Department of Food Science
North Carolina State University, Raleigh, N. C. 27607

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